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(54) Title: **PROCESS FOR PRODUCING DURABLE ANTIREFLECTIVE SURFACES AND ANTIREFLECTIVE ARTICLES**

## (57) Abstract

The invention describes a process for improving the durability of porous antireflective surfaces without significantly effecting the percent reflectance of the coated surface. The process includes the steps of applying and curing a "compatible" coating composition to the porous antireflective surface and applying and curing a hydrophobic coating composition to the cured "compatible" coating. The "compatible" coating composition contains at least one tetraalkyl orthosilicate, at least one metal oxide sol and optionally a catalyst. The hydrophobic coating composition comprises an amorphous fluoropolymer, perfluoroalkyl organosilane and solvent.

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PROCESS FOR PRODUCING DURABLE ANTIREFLECTIVE  
SURFACES AND ANTIREFLECTIVE ARTICLES

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DESCRIPTION OF THE INVENTION

The present invention relates to a process which improves the durability of a porous antireflective coating. More specifically, the present invention relates to 10 antireflective coatings that are more adherent and abrasion resistant. Still more particularly, this invention relates to solid articles having a durable antireflective coating on at least one surface.

It is known that reducing glare on reflective 15 surfaces such as optical articles or elements, e.g., windows, ophthalmic lenses, transparent sheets, films, display surfaces, and the like, is desirable. The amount of reflected light from such surfaces can be reduced by means of an antireflective coating. The advantages of such coatings, as 20 reported by K. H. Guenther in *Thin film coating Technology for Ophthalmic Lenses*, SPIE, 601, Ophthalmic Optics, 1985, pages 67-87, are the elimination of ghost images due to multiple internal reflections, and of disturbing reflection to the wearer and the external viewer. As a consequence, the wearer 25 not only sees better, but also looks better.

Porous antireflective coatings have been disclosed in numerous U.S. Patents. Examples of such patents include U.S. Patents 4,273,826; 4,830,879, 5,116,644; 5,580,819 and 5,723,175. U.S. Patent 4,273,826 describes the process of 30 forming a thin glass film on a substrate, heating the film to cause phase separation and etching and leaching the film to preferentially dissolve one of the phases. This process

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results in a skeletonized surface film having a graded refractive index. U.S. Patent 4,830,879 describes the process of preparing and depositing on a substrate a series of polymeric solutions of alkoxy compounds, each containing 5 particles of increasing size. This process produces a microporous coating characterized by graded particles and hence graded porosity across the coating thickness. U.S. Patent 5,116,644 describes the process of coating a plastic lens with a siloxane-containing solution having at least one 10 oxide sol, curing and immersing the coated lens into an acidic or alkaline solution to dissolve the oxide particles. This process results in a non-uniform coating having a graded refractive index. U.S. Patent 5,580,819 describes the process of applying a durable coating composition to a solid 15 substrate, curing and treating the cured coating with an aqueous electrolyte solution for a time sufficient to produce a coating having graded porosity. U.S. Patent 5,723,175 describes a method of imparting antireflective and anti- 20 fogging properties to a substrate by applying a coating composition of inorganic metal oxide in combination with particular anionic silanes.

Antireflective coatings formed by the dissolution of components within the coating using various treatment chemicals, e.g., acids, bases and electrolytes, may undergo 25 further dissolution during use of the antireflective article. For example, chemical attack of such antireflective surfaces may result from exposure to acid rain and various cleaning agents which may be acidic or alkaline. It is also known that such porous coatings have very poor mechanical strength and 30 are particularly sensitive to physical contact, e. g., wiping with a dry cloth. Consequently, there is a need to improve

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the durability, i.e., the adhesion and abrasion resistance, of such antireflective coatings.

The use of metal oxides and trialkoxysilanes in protective coatings has been disclosed in U.S. Patent 5 3,986,997. A broad range of metal oxide particle sizes is disclosed without consideration of the need to match metal oxide particle size and coating composition compatibility with the surface being treated.

The use of amorphous fluoropolymer in coatings has been disclosed in U.S. patent 5,467,717 and Japanese Patent Publication 61/36230. U.S. Patent 5,467,717 describes a process for depositing an antireflective, hydrophobic and abrasion resistant coating on a substrate. The hydrophobic coating is amorphous fluoropolymer dissolved in a perfluorinated solvent. JP 61/36230 describes fluoropolymer coatings with improved adhesion comprising amorphous fluoropolymers and amino silanes in perfluorinated solvents. Neither patent describes the use of perfluoroalkyl organosilane in coating solutions of amorphous fluoropolymers and perfluorinated solvent.

It has now been discovered that applying a further coating composition that is compatible with the porous antireflective coating and that contains at least one metal oxide sol, at least one tetraalkyl orthosilicate and an optional catalyst to the antireflective coating results in an antireflective surface having improved durability. It has also been discovered that the abrasion resistance of the aforementioned durable antireflective surface may be improved by the application of a hydrophobic coating composition, such as a composition of an amorphous fluoropolymer, perfluoroalkyl organosilane and a perfluorinated solvent to the further coating composition.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention is an improved process for increasing the durability of porous antireflective (AR) coatings. As used in this specification and claims, porous antireflective coatings are antireflective coatings having pores or openings in the coatings. Such pores may have resulted from the removal of coating components by methods such as etching, leaching and/or dissolving to produce pores of a size sufficient to render the coating antireflective or from the process used to produce the antireflective coating. For example, coatings formed by the sol-gel (solution-gelation) process are porous throughout due to voids present between the metal oxide particles.

Preferably, the porous antireflective coating is one having graded porosity, i.e., the porosity of the antireflective coating decreases through the thickness of the AR coating along a path starting at a point on the top of the AR coating and proceeding to a point adjacent to the substrate to which the AR coating is applied. Stated another way, the density of the AR coating increases going from the top to the bottom of the AR coating. Methods for producing antireflective coatings having a graded porosity are disclosed in U.S. Patents 4,273,826; 4,535,026; 4,830,879, 5,116,644; 5,572,086, 5,580,819 and 5,723,175, the disclosures of which are incorporated herein *in toto* by reference.

In accordance with the present process, a further or second coating composition that is compatible with the antireflective coating and that comprises at least one metal oxide sol, at least one tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate and optionally a catalyst is applied to the porous AR coating. By

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the term "compatible", is meant that the second coating does not significantly reduce the percent reflectance of the antireflective coating. The reduction in percent reflectance after cleaning should not exceed 30% of the initial value, as 5 measured by the Cleanability Test described in Part B of Example 4 of this description, preferably not more than 20% and most preferably not more than 10%. For example, if the initial percent reflectance of the antireflective coating is 2%, the percent reflectance should not be less than 1.4% after 10 applying and curing the second coating and subjecting the resultant coated surface to the Cleanability Test.

Procedures for making the surface of a substrate antireflective typically cause a significant reduction in percent reflectance, e.g., from 8 percent for an uncoated 15 polymerizate of CR-39® monomer to a level at or below 2 percent for the AR coated polymerizate. This results in a reduction of the percent reflectance of 75 percent. The process of the present invention may also be used to modify, i.e., increase or decrease, the percent reflectance of the AR 20 coating to produce a desired reflected color. These modifications are accomplished by varying the thickness of the applied coating, e.g., a thickness of 50 to 75 nm produces a gold color (3 percent reflectance), while a thickness of 75 to 125 nm produces a purple color (1.5 percent reflectance) and a 25 thickness of 125 to 150 nm produces a blue color (3 percent reflectance).

The process of the present invention further comprises the steps of applying and curing on the second coating a hydrophobic coating composition. Any type of 30 hydrophobic coating that results in a durable water repellent surface is suitable. Preferably, the hydrophobic coating is optically clear for the purposes of looking through to the

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substrate surface or for retaining the underlying aesthetic features of the substrate surface. Examples of commercially available hydrophobic coatings include those obtained with the AQUAPEL® GLASS TREATMENT (available from PPG Industries, 5 Inc.), ZONYL® TM fluoromonomer (E. I. duPont de Nemours and Company) and CRYSTALON® hydrophobic coating (available from Nanofilm, Inc.). The preferred hydrophobic coating composition is one that improves the abrasion resistance of the surface and comprises an amorphous fluoropolymer, 10 perfluoroalkyl organosilane, perfluorinated solvent and optionally a hydrolyzable silane or siloxane.

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be 15 understood as modified in all instances by the term "about". In each instance where the term "weight percent" is used herein with respect to a coating composition, it is to be understood that the described weight percent is based on the total weight of the coating composition.

20 The metal oxide sol that may be used in the further coating of the present invention is a material that improves the durability of the base AR coating without effecting its transmission/reflectance. As used in the present specification and claims, by the term sol is meant a colloidal 25 dispersion of finely divided solid inorganic metal oxide particles in an aqueous or an organic liquid. Such metal oxide sols may be prepared by hydrolyzing a metal salt precursor for a time sufficient to form the desired particle size or such sols may be purchased commercially. Stable 30 acidic and alkaline metal oxide sols are commercially available as aqueous dispersions. Metal oxide sols may also

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be obtained as dispersions in organic liquids, e.g., ethanol, isopropyl alcohol, ethylene glycol and 2 propoxyethanol.

Examples of commercially available metal oxide sols that may be used in the composition of the present invention 5 include NALCO® colloidal sols (available from NALCO Chemical Co.), REMASOL® colloidal sols (available from Remet Corp.) and LUDOX® colloidal sols (available from E. I. du Pont de Nemours Co., Inc.). These products are characterized by their average 10 particle size, particle size distribution, surface area, pH, specific gravity, viscosity, stabilizing ion, approximate percentage of Na<sub>2</sub>O, and surface charge. One or more of these physical/chemical characteristics will be taken into 15 consideration when evaluating the "compatibility" of the further coating composition with the antireflective surface to which it is applied.

The metal oxide may be selected from the group consisting of silica, i.e., silicon dioxide, aluminum oxide, antimony oxide, tin oxide, titanium oxide, zirconium oxide and mixtures thereof, and preferably is silica. Most preferably, 20 the metal oxide sol is an acid stabilized colloidal silica.

The particle size of the metal oxide sol used is a size that does not significantly reduce the percent reflectance of the antireflective surface as measured in the Cleanability Test described in Part B of Example 4. In most 25 cases, the metal oxide sol should be of a narrow particle size distribution, such as from 10 to 12 or from 17 to 22 nanometers, rather than a broad particle size distribution, e.g., from 10 to 50 nanometers. In some cases, the metal oxide sol may be a mixture of specific narrow particle size 30 distributions, e.g., from 2 to 4 and from 10 to 12 nanometers. Therefore, it is necessary to evaluate the metal oxide sol to determine if the size or another characteristic of the

selected sol results in a "compatible" coating composition as defined herein.

The average particle diameter of the metal oxide sol used in the present invention is typically less than 80 5 nanometers, preferably less than 50 nanometers and more preferably is 30 nanometers or less, e.g., nominally 2, 5, 10, 15, 20, 25 or 30 nanometers, and most preferably is nominally 20 nanometers. Stated differently, the nominal particle size may vary preferably from 2 to 30, more preferably from 2 to 10 20, nanometers. Preferably, the particle size distribution falls within  $\pm$  30 percent of the average particle diameter, e.g., a metal oxide sol having an average particle diameter of 20 nm has a particle size distribution of from 14 to 26 nm. More preferably, the particle distribution falls within  $\pm$  20 15 percent, and most preferably, it falls within  $\pm$  10 percent of the average particle diameter.

The amount of metal oxide sol used in the coating composition of the present invention relative to the amount of tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate can vary. More particularly, 20 the weight ratio, based on solids, of metal oxide sol:tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate solids may range from 1:1 to 9:1, preferably from 1.5:1 to 4:1 and more preferably 2.3:1, i.e., 70:30. The solids level of the metal oxide sol is the amount of metal oxide particles in the dispersion. 25 Commercially available colloidal sols are sold as sols having a specific percent solids level based on the metal oxides. For example, Nalco 1034A has 34 percent silica as SiO<sub>2</sub>. In calculating the percent solids for a tetraalkyl orthosilicate, the molecular weight of the silanol formed is taken into 30 account. The solids level for the tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate is calculated as the percent of the silanol that theoretically forms during hydrolysis of the orthosilicate.

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For example, tetramethyl orthosilicate, i.e.,  $\text{Si}(\text{OCH}_3)_4$ , has a molecular weight of 152. The molecular weight of the silanol that is formed, i.e.,  $\text{Si}(\text{OH})_4$ , during hydrolysis is 96. Therefore, the theoretical percent solids of tetramethyl 5 orthosilicate is 63.

Suitable tetra(( $\text{C}_1\text{-C}_4$ )alkyl) orthosilicates that may be used in the process of the present invention include materials such as tetramethyl orthosilicate, tetraethyl orthosilicate, tetrapropyl orthosilicate, tetrabutyl 10 orthosilicate and mixtures thereof. Most preferably, tetramethyl orthosilicate is used.

Suitable materials that may be used as the optional catalyst include: organic amines such as triethylamine, n-butylamine, etc.; amino acids such as glycine, etc.; metal 15 acetylacetones such as aluminum acetylacetone, chromium acetylacetone, titanium acetylacetone, cobalt acetylacetone, etc.; metal salts of organic acids such as sodium acetate, zinc naphthenate, cobalt naphthenate, zinc caprylate, tin caprylate, etc.; Lewis acids such as stannic 20 chloride, ferric chloride, titanium chloride, zinc chloride, antimony chloride, etc.; and mixtures thereof. Among these catalysts, aluminum acetylacetone is preferred. The amount of catalyst used is a catalytic amount, i.e., an amount necessary to catalyze or enhance the curing of the coating 25 composition. This amount may range from 0.01 to 5.0 weight percent.

A solvent is also present as a component in the further coating composition. The amount of solvent used is a solvating amount, i.e., the amount necessary to dissolve 30 and/or disperse the components of the coating composition and serve as a vehicle for applying the coating composition. Any solvent that accomplishes these tasks and enables a more durable antireflective surface to be prepared by the process of this invention is suitable. The preferred solvent is a

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lower aliphatic alcohol solvent. The lower aliphatic alcohol solvent as used herein and in the claims may be represented by the formula  $[(R^3)_i R^4]_j (C_1-C_3)OH$ , wherein  $R^3$  and  $R^4$  are each  $C_1-C_2$  alkoxy and  $i$  and  $j$  are each the integers 0 or 1.

5 Preferably, the solvent is a  $C_1-C_3$  alkanol or an aliphatic alcohol of the formula  $[(R^3)_i R^4]_j (C_1-C_3)OH$ , wherein  $j$  is 1, and  $i$  is 0 or 1. Such solvents may be selected from the group consisting of methanol, ethanol, 2-ethoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-methoxyethanol, 2-(2-ethoxymethoxy)ethanol, 1-propanol, 2-propanol, and 1-methoxy-2-propanol. Preferred solvents may be selected from the group consisting of methanol, ethanol, 1-propanol, and 1-methoxy-2-propanol. The most preferred solvents are methanol, ethanol and 1-propanol.

15 The further coating composition may also contain a surfactant as described in U.S. Patent 5,580,819, column 7, line 32 to column 8, line 46, which disclosure is incorporated herein by reference.

The further coating composition of the present invention may further comprise additional conventional ingredients/adjuvants which impart desired properties to the composition, which are required for the process used to apply and cure the composition, or which enhance the cured coating made therefrom. Such additional ingredients/adjuvants comprise rheology control agents, initiators, cure-inhibiting agents, free radical scavengers and adhesion promoting agents, such as trialkoxysilanes that preferably have an alkoxy substituent of 1 to 4 carbon atoms, including  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -aminopropyltrimethoxysilane, 3,4-epoxycyclohexylethyl-trimethoxysilane and aminoethyltrimethoxysilane.

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The coating composition of the present invention may be prepared by selecting a metal oxide sol and other components that are compatible with the antireflective surface to be coated, adding the selected amount, based on solids, of 5 the metal oxide sol to the tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate and mixing until the metal oxide sol appears to be uniformly dispersed. To this dispersion is added the solvent and optional catalyst to produce the coating composition of the present invention. The resulting mixture is stirred and 10 maintained at room temperature until the orthosilicate is completely hydrolyzed. Prior to use as a coating composition, the mixture is filtered through a suitable filter, such as a 0.45 capsule filter. The resulting solids level may range from 1 to 50 weight percent, preferably 2 to 10 weight percent 15 and most preferably from 4 to 6 weight percent, e.g., 5 weight percent. The percent solids of the coating composition may also be adjusted outside of the specified range depending on how the coating composition will be applied.

Following application of the coating composition to 20 the antireflective surface, the coating is cured. For handling purposes, the coated AR surface may be dried first and then cured. The coating may be dried at ambient temperatures or temperatures above ambient but below curing temperatures, e.g., up to 80°C. Afterwards, the dried, coated 25 AR surface is heated to a temperature of between 80°C and 130°C, e.g., 120°C, for a period of from 30 minutes to 16 hours in order to cure the coating. While a range of temperatures has been provided for drying and curing the coating, it will be recognized by persons skilled in the art 30 that temperatures other than those disclosed herein may be used. Additional methods for curing the coating include

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irradiating it with infrared, ultraviolet, gamma or electron radiation.

The coating composition may be applied to the antireflective surface using a coating process such as that 5 described in U.S. Patent 3,971,872, the disclosure of which is incorporated herein by reference. Any suitable conventional coating method may be used. To achieve optimum results in a dip coating process, a uniform, vibration-free withdrawal of the substrate to be coated is necessary. Vibration of the 10 substrate at the air/liquid interface during withdrawal will prevent application of a uniform coating. It is also recommended that continuous filtration of the coating composition through a 0.45 micron filter with recirculation through a dam be done to minimize particulate matter.

15 Conventional coating methods include flow coating, dip coating, spin coating, roll coating, curtain coating and spray coating. Application of the coating may be done in an environment that is substantially free of dust or contaminants, e.g., a clean room. Coatings prepared by the 20 process of the present invention may range in thickness from 5 to 250 nanometers, preferably from 50 to 150 nm, and more preferably from 75 to 125 nm, e.g., 100 nm.

The present invention also includes the application and curing of a durable hydrophobic coating to the coated 25 antireflective surface. The hydrophobic coating should be optically clear, adhere to the further coating, provide a water repelling surface and improve the abrasion resistance of the coated substrate. Examples of such hydrophobic coatings include the commercially available coatings obtained with 30 AQUAPEL® GLASS TREATMENT, ZONYL® TM fluoromonomer and CRYSTALON® hydrophobic coating. Preferably, the hydrophobic coating comprises a composition of (1) an amorphous

fluoropolymer, such as TEFLON® AF amorphous fluoropolymer, which is disclosed in U.S. Patent 4,754,009, (2) a water repelling agent comprising perfluoroalkyl organosilane and optionally a hydrolyzable silane or siloxane, which water repelling agent is disclosed in U.S. Patents 4,983,459; 4,997,684; 5,308,705; 5,328,768; 5,523,161; 5,523,162; 5,674,967; 5,688,684 and 5,707,740, and (3) a solvent in which the amorphous fluoropolymer is soluble, such as a perfluorinated solvent, e.g., FLUORINERT® solvents FC40 and 75 (available from 3M Co.). The disclosures of the aforementioned patents relating to the components of the hydrophobic coating composition are incorporated herein *in toto* by reference.

Perfluoroalkyl organosilanes that are preferred for use in the practice of the present invention have the general formula  $R_mR'_nSiX_{4-m-n}$ , wherein R is a perfluoroalkyl radical; R' is a vinyl or an alkyl radical; X is a radical such as halogen, acyloxy, and/or alkoxy; m is 1, 2 or 3; n is 0, 1 or 2; and m+n is less than 4. Preferred perfluoroalkyl moieties in the perfluoroalkyl radicals range from  $CF_3$  to  $C_{30}F_{61}$ , preferably  $C_6F_{13}$  to  $C_{18}F_{37}$ , and most preferably  $C_8F_{17}$  to  $C_{12}F_{25}$ ; R' is preferably a methyl, ethyl, vinyl or propyl and more preferably is methyl or ethyl. Preferred radicals for X include hydrolyzable chloro, bromo, iodo, methoxy, ethoxy and acetoxy radicals. Preferred perfluoroalkyl organosilanes in accordance with the present invention include perfluoroalkylethyltrichlorosilane, perfluoroalkylethyltrimethoxysilane, perfluoroalkylethyltriacetoxy silane, perfluoroalkylethyldichloro(methyl)silane and perfluoroalkylethyldiethoxy(methyl)silane.

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Suitable hydrolyzable silanes have the general formula  $\text{SiX}_4$  wherein X is a hydrolyzable radical that is generally selected from the group consisting of halogens, alkoxy and acyloxy radicals. Preferred silanes are those 5 wherein X is chloro, bromo, iodo, methoxy, ethoxy and acetoxy. Preferred hydrolyzable silanes include tetrachlorosilane, tetramethoxysilane and tetraacetoxy silane.

Suitable siloxanes have the general formula  $\text{Si}_y\text{O}_z\text{X}_{4y-2z}$ , wherein X is selected from halogen, alkoxy and 10 acyloxy radicals, y is at least 2, and z is at least 1 and  $4y-2z$  is greater than zero. Preferred hydrolyzable siloxanes include hexachlorodisiloxane, octachlorotrisiloxane and higher oligomer chlorosiloxanes.

The hydrophobic coating composition may be prepared 15 by adding from 0.01 to 0.5 weight percent of amorphous fluoropolymer and from 0.1 to 5.0 weight percent of the water repelling agent to the perfluorinated solvent, and mixing until all of the components are dissolved. Preferably, the amount of amorphous fluoropolymer used is from 0.1 to 0.3 20 weight percent, the amount of water repelling agent is from 0.3 to 3.0 weight percent and the amount of solvent is a solvating amount, i.e., the amount necessary to dissolve all of the components. Typically, the amount of solvent ranges from 96.7 to 99.6 weight percent. The amount of solvent may 25 vary outside of this range depending on the desired solids level, coating thickness and application method used. The resulting coating composition may be applied to the coated antireflective surface using the aforementioned application methods. The hydrophobic coating composition may also contain 30 a leveling amount of surfactant and the additional conventional ingredients/adjuvants, which were listed previously for the further coating composition.

The thickness of the hydrophobic coating should be a thickness that results in the coated surface having improved abrasion resistance, as measured in ASTM Test Method F735-81. The thickness of the coating should also result in a 5 "compatible" coating, i.e., the hydrophobic coating does not significantly reduce the percent reflectance of the antireflective coating. The thickness of the hydrophobic coating may range from a monomolecular layer to 250 nanometers, more preferably, from a monomolecular layer to 100 10 nanometers, preferably, from a monomolecular layer to 50 nm, e.g., from 1 to 40 nanometers.

The substrates having AR coatings to which the coating composition of the present invention may be applied include: glass, quartz, metals, ceramics, and solid organic 15 polymeric materials. Examples of organic polymeric materials include polymers, i.e., homopolymers and copolymers, of polyol(allyl carbonate) monomers, diethylene glycol dimethacrylate monomers, diisopropenyl benzene monomers, and alkoxylated polyhydric alcohol acrylate monomers, such as 20 ethoxylated trimethylol propane triacrylate monomers, polymers, i.e., homopolymers and copolymers, of polyfunctional, i.e., mono-, di-, tri-, or tetra- functional, acrylate and/or methacrylate monomers, polyacrylates, polymethacrylates, poly(C<sub>1</sub>-C<sub>12</sub>) alkylacrylates such as a 25 poly(methyl methacrylate), polyoxy (alkylene methacrylates) such as poly(ethylene glycol bis methacrylates), poly(ethoxylated phenol methacrylates), such as poly(ethoxylated bisphenol A dimethacrylates) cellulose acetate, cellulose triacetate, cellulose acetate propionate, 30 cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene chloride), polyurethanes, polytiourethanes, thermoplastic polycarbonates,

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polyesters, poly(ethylene terephthalate), polystyrene, copoly(styrene-methyl methacrylates) copoly(styrene-acrylonitrile), polyvinylbutyral and polymers, i.e., homopolymers and copolymers, of diallylidene pentaerythritol, 5 particularly copolymers with polyol(allyl carbonate) monomers, e.g., diethylene glycol bis(allyl carbonate), and acrylate monomers.

Transparent copolymers and blends of transparent polymers are suitable as substrates for AR coated optical 10 articles to which the coating composition of the present invention may be applied. Preferably, the substrate is an optically clear polymerized organic material prepared from a thermoplastic polycarbonate resin, such as the carbonate-linked resin derived from bisphenol A and phosgene, which is 15 sold under the trademark LEXAN; a polyester, such as the material sold under the trademark MYLAR; a poly(methyl methacrylate), such as the material sold under the trademark PLEXIGLAS; polymerizates of a polyol(allyl carbonate) monomer, especially diethylene glycol bis(allyl carbonate), which 20 monomer is sold under the trademark CR-39, and polymerizates of copolymers of a polyol (allyl carbonate), e.g., diethylene glycol bis(allyl carbonate), with other copolymerizable monomeric materials, such as copolymers with vinyl acetate, and copolymers with a polyurethane having terminal diacrylate 25 functionality, as described in U.S. Patent 4,360,653 and 4,994,208; and copolymers with aliphatic urethanes, the terminal portion of which contain allyl or acrylyl functional groups, as described in U.S. Patent 5,200,483; poly(vinyl acetate), polyvinylbutyral, polyurethane, polythiourethane and 30 polymers of members of the group consisting of diethylene glycol dimethacrylate monomers, diisopropenyl benzene monomers, and ethoxylated trimethylol propane triacrylate

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monomers; cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, polystyrene and copolymers of styrene with methyl methacrylate, vinyl acetate and acrylonitrile.

5           The organic polymeric material may be in the form of optical elements such as windows, plano and vision correcting ophthalmic lenses, exterior viewing surfaces of liquid crystal displays, cathode ray tubes e.g., video display tubes for televisions and computers, clear polymeric films, automotive 10 transparencies, e.g., windshields, aircraft transparencies, plastic sheeting, etc. Application of the coatings of the present invention to an antireflective polymeric film in the form of an "applique" may be accomplished using the methods described in column 17, line 28 to column 18, line 57 of U.S. 15 Patent 5,198,267.

          In a first contemplated embodiment of the present invention, a glass surface having a percent reflectance of 2.5, that was made antireflective by the process of U. S. Patent 4,273,826, is dip-coated with a coating composition of 20 the present invention. The rate of extraction is adjusted to result in a cured coating having a thickness of 150 nanometers. The coating on the antireflective glass surface is cured for 30 minutes at 120°C. The percent reflectance after the Cleanability test is 3.0 resulting in a reflected 25 blue color.

          In another contemplated embodiment of the present invention, a plastic surface having a percent reflectance of 1.5, that was made antireflective by the process of U. S. Patent 5,580,819, is dip-coated with a coating composition of 30 the present invention. The rate of extraction is adjusted to result in a cured coating having a thickness of 100 nanometers. The coating on the plastic is cured for 30

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minutes at 120°C. The percent reflectance after the Cleanability test is unchanged and results in a reflected purple color. A hydrophobic coating composition of the present invention is applied by spraying and cured by heating 5 for 30 minutes at 120°C. The reflected color remains unchanged.

The present invention is more particularly described in the following examples which are intended as illustrative only, since numerous modifications and variations therein will 10 be apparent to those skilled in the art.

EXAMPLE 1

NALCO® 1034A (161.5 grams), an acid stabilized colloidal silica having a particle size of 20 nm, and 15 tetramethylorthosilicate (38.5 grams) were added to a reaction flask. The resulting solution was stirred for 30 minutes. Ethanol (1375 grams) and aluminum acetyl acetonate (0.9 grams) were added to the reaction flask. The solution was stirred for an additional 30 minutes and filtered using a 0.45 micron 20 capsule filter.

Example 2

The procedure of Example 1 was followed except that the amount of NALCO® 1034A colloidal silica used was doubled. 25 This resulted in a coating composition having 5 weight percent solution solids based on the weight of the total coating composition.

EXAMPLE 3

30 TEFLON® AF 1600 (4.5 grams) and material purchased as AQUAPEL® GLASS TREATMENT (15 grams) were added to a beaker containing FLUORINERT® FC 75 (3,000 grams), reported to be

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perfluorobutyl tetrahydrofuran, and stirred for about 16 hours at ambient temperature.

Comparative Example 1

5 The procedure of Example 1 was followed except that NALCO® 1040, an alkaline stabilized colloidal silica having a particle size of 20 nm, was used in place of NALCO® 1034A.

Comparative Example 2

10 The procedure of Example 1 was followed except that LUDOX® acid stabilized colloidal silica having a particle size of 12 nm was used in place of NALCO® 1034A.

EXAMPLE 4

15

PART A

Test samples of 75-80 mm diameter, 6 plano finished, single vision lenses prepared from CR-39® diethylene glycol bis(allyl carbonate)monomer having a porous antireflective surface, which was prepared substantially as described in Examples 1 and 12 of U.S. Patent 5,580,819, were used. The coating compositions of Examples 1 and 2 and Comparative Examples 1 and 2 were applied to the test samples by dip-coating. The withdrawal rate used was approximately 10 to 15 centimeters per minute. Afterwards, the coated test samples were dried and cured in an air-circulating oven for 30 minutes at 120°C. Test samples having the porous antireflective coatings of the '819 patent were used as Controls.

The hydrophobic coating composition of Example 3 was applied by dip-coating to test samples having the cured coating of Example 1. The aforementioned withdrawal rate and curing conditions were used in preparing the test samples coated with the hydrophobic coating.

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Part B

Test samples prepared in Part A and coated with the coating composition of Example 1 and the Control samples were 5 evaluated in the Cleanability Test. The Cleanability Test comprises determining the percent reflectance prior to dry wiping, after dry wiping 15 times and after dry wiping another 15 times for a total of 30 times with a low-lint paper towel, 10 e.g., KIMWIPES EX-L. The lenses were wiped back and forth for each counted wipe.

In order to simulate actual use conditions, skin oil collected from the face, i.e., the surface of the front of the head from the top of the forehead to the base of the chin and from ear to ear, may be smeared on the coated AR surface prior 15 to wiping. After wiping and prior to reflectance testing, the smeared oil may be removed with isopropyl alcohol. Percent reflectance was measured with a SHIMADZU UV/Sis Scanning Spectrophotometer Model No. 2101 PC. For the purpose of determining a significant reduction in percent reflectance, 20 wiping back and forth 15 times is the requirement of the Cleanability Test. The results are listed in Table 1.

Part C

Test samples prepared in Part A were tested for 25 percent reflectance before and after being coated with the coating compositions of Example 2 and Comparative Examples 1 and 2. The results listed in Table 2 are a numerical average of readings on 4 lenses per treatment.

30

Part D

Abrasion resistance of test samples prepared in Part A having the cured coating composition of Example 1 and test

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samples having successively applied thereon the coating compositions of Example 1 and Example 3 was determined. ASTM Test Method F735-81 was used. The test samples were exposed to 300 cycles of oscillation in the ASTM Test Method. The 5 Bayer Abrasion Resistance Index (BARI), listed in Table 3, was calculated by dividing the difference in the percent haze before and after the ASTM Test Method of an uncoated test sample made of a homopolymer prepared from CR-39® monomer by the difference in the percent haze of the coated test sample. 10 The resulting number is an indication of how much more abrasion resistant the coated test sample is as compared to the uncoated test sample. The BARI, listed in Table 3, is a numerical average of results from duplicate tests. The haze and transmission results before and after abrasion testing 15 were measured with a Hunter Lab Model DP25P Colorimeter.

Table 1

Coating Composition	Percent Reflectance (Initial)	Percent Reflectance (After 15 wipes)	Percent Reflectance (After 30 wipes)
Example 1	2.08	1.94	---
Example 1	2.64	2.67*	2.69*
Control	1.55	1.97	2.11

20 \*The coated antireflective surface was smeared with skin oil prior to wiping. The oil was removed by rinsing with isopropyl alcohol prior to reflectance testing.

The results of Table 1 show that the lenses coated with the composition of Example 1, which lenses were coated 25 and tested at different times and may have varied in coating thickness, either decreased or showed a slight increase in percent reflectance after cleaning. The Control lenses having

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the porous antireflective coating demonstrated a significant increase in percent reflectance after 15 wipes and a further increase after a total of 30 wipes. The increase in percent reflectance is attributed to a loss of the antireflective 5 layer.

Table 2

Coating Composition	Percent Reflectance (Initial)	Percent Reflectance (with Coating)
Example 2	1.85	1.65
CE 1	1.85	2.61
CE 2	1.85	5.86

The results of Table 2 show that the AR lenses coated with the coating composition of Example 2 demonstrated 10 a decrease in percent reflectance as compared to the initial result for the uncoated antireflective surface. The lenses coated with the coating compositions of Comparative Examples 1 and 2 showed significant increases in percent reflectance indicating a loss of antireflectivity.

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Table 3

Coating Compositions	BARI
Example 1	1.27
Example 1/Example 3	1.79

The results of Table 3 show that the lenses coated with the coating composition of Example 1 are less resistant 20 to abrasion than similarly coated lenses having the additional hydrophobic coating of Example 3.

Although the present invention has been described with reference to the specific details of particular

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embodiments thereof, it is not intended that such details be regarded as limitations upon the scope of the invention except as and to the extent that they are included in the accompanying claims.

5

We claim:

1. A method of improving the durability of a  
5 porous antireflective surface, comprising applying to said  
surface a coating composition comprising at least one metal  
oxide sol and at least one tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate,  
the weight ratio, based on solids, of said metal oxide sol to  
said orthosilicate being from 1:1 to 9:1, and curing said  
10 applied coating, said cured coating being such that it does  
not reduce significantly the percent reflectance of the porous  
antireflective surface.

2. The method of claim 1 wherein the metal oxide  
15 has an average particle diameter less than 80 nanometers.

3. The method of claim 2 wherein the average  
particle diameter is 20 nanometers.

20 4. The method of claim 1 wherein the metal oxide  
sol is a sol of a metal oxide selected from the group  
consisting of silicon dioxide, aluminum oxide, antimony oxide,  
tin oxide, titanium oxide, zirconium oxide and mixtures  
thereof.

25 5. The method of claim 4 wherein the metal oxide  
sol is silicon dioxide sol.

6. The method of claim 5 wherein the silicon  
30 dioxide sol is acid stabilized.

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7. The method of claim 1 wherein the tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate is selected from the group consisting of tetramethyl orthosilicate, tetraethyl orthosilicate, tetrapropyl orthosilicate, tetrabutyl orthosilicate and 5 mixtures thereof.

8. The method of claim 7 wherein the tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate is tetramethyl orthosilicate.

10 9. The method of claim 1 wherein the ratio of metal oxide sol: tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl] orthosilicate ranges from 1.5:1 to 4:1.

15 10. The method of claim 9 wherein the ratio is 2.3:1.

11. The method of claim 1 wherein the coating composition further comprises catalyst for enhancing the curing of said coating composition.

20 12. The method of claim 11 wherein the catalyst is selected from the group consisting of organic amines, amino acids, metal acetylacetones, metal salts of organic acids, Lewis acids and mixtures thereof.

25 13. The method of claim 12 wherein the catalyst is aluminum acetylacetone.

14. The method of claim 1 further comprising the 30 steps of applying and curing a durable hydrophobic coating composition to the applied coating.

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15. The method of claim 14 wherein the hydrophobic coating composition comprises amorphous fluoropolymer, perfluoroalkyl organosilane, and solvent.

5 16. The method of claim 15 wherein the perfluoroalkyl organosilane is selected from the group consisting of perfluoroalkylethyltrichlorosilane, perfluoroalkylethyltrimethoxysilane, perfluoroalkylethyltriacetoxysilane, 10 perfluoroalkylethyldichloro(methyl)silane, perfluoroalkylethyldiethoxy(methyl)silane and mixtures thereof.

15 17. The method of claim 15 wherein the hydrophobic coating composition further comprises a hydrolyzable silane or siloxane.

20 18. The method of claim 17 wherein the hydrolyzable silane is selected from the group consisting of tetrachlorosilane, tetramethoxysilane and tetraacetoxysilane.

25 19. The method of claim 17 wherein the hydrolyzable siloxane is selected from the group consisting of hexachlorodisiloxane, octachlorotrisiloxane and higher oligomer chlorosiloxanes.

20. A method of improving the durability of a porous antireflective coated surface, comprising:

30 a) applying to said surface a coating composition comprising:

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- (i) acid stabilized silicon dioxide sol having an average particle diameter of 20 nanometers;
- 5 (ii) tetramethyl orthosilicate; and
- (iii) a catalytic amount of aluminum acetylacetone; wherein the weight ratio, based on solids, of (i):(ii) is 2.3:1;
- b) curing the applied coating; provided said cured coating does not reduce significantly the percent reflectance of the porous antireflective surface; and
- 10 c) applying and curing a hydrophobic coating composition comprising:
  - (i) amorphous fluoropolymer;
  - 15 (ii) perfluoroalkyl organosilane;
  - (iii) hydrolyzable silane or siloxane and
  - (iv) perfluorinated solvent.

21. In an article having, in combination, a solid  
20 substrate and on at least one surface thereof a porous antireflective surface, wherein the improvement comprises a first coating on said antireflective surface of the hydrolysis and condensation reaction product of (i) metal oxide sol and (ii) tetra[(C<sub>1</sub>-C<sub>4</sub>)alkyl]orthosilicate, the weight ratio of  
25 (i):(ii), based on solids, being from 1:1 to 9:1, said first coating being such that it does not reduce significantly the percent reflectance of the porous antireflective surface.

22. The article of claim 21 wherein the  
30 improvement further comprises a durable hydrophobic coating applied to the first coating.

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23. An article comprising, in combination, a solid substrate, a porous antireflective coating on at least one surface thereof, and

(a) a first coating on said antireflective coating comprising the hydrolysis and condensation reaction product of:

5 (i) an acid stabilized silicon dioxide sol having an average particle diameter of 20 nanometers;

10 (ii) tetramethyl orthosilicate; and

15 (iii) a catalytic amount of aluminum acetylacetone, the weight ratio, based on solids, of (i):(ii) being 2.3:1, said first coating being such that it does not reduce significantly the percent reflectance of the porous antireflective coating; and

15 (b) a durable hydrophobic second coating on said first coating comprising the cured reaction product of:

20 (i) amorphous fluoropolymer;

(ii) perfluoroalkyl organosilane;

(iii) hydrolyzable silane or siloxane; and

(iv) perfluorinated solvent.

25 24. The article of claim 21 wherein the substrate is selected from the group consisting of glass, quartz, ceramic, metal, and solid organic polymeric material.

30 25. The article of claim 24 wherein the solid organic polymeric material is selected from the group consisting of polyacrylates, polymethacrylates, poly(C<sub>1</sub>-C<sub>12</sub>) alkyl methacrylates, polyoxy(alkylene methacrylates), poly

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(alkoxylated phenol methacrylates), cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene chloride), thermoplastic 5 polycarbonates, polyesters, polyurethanes, polythiourethanes, poly(ethylene terephthalate), polystyrene, poly(alpha methylstyrene), copoly(styrene-methylmethacrylate), copoly(styrene-acrylonitrile), polyvinylbutyral and polymers of members of the group consisting of polyol(allyl carbonate) 10 monomers, polyfunctional acrylate monomers, polyfunctional methacrylate monomers, diethylene glycol dimethacrylate monomers, diisopropenyl benzene monomers, alkoxyated polyhydric alcohol monomers and diallylidene pentaerythritol monomers.

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26. The article of claim 25 wherein the solid organic polymeric material is a homopolymer or copolymer of monomer(s) selected from the group consisting of acrylates, methacrylates, methyl methacrylate, ethylene glycol bis 20 methacrylate, ethoxylated bisphenol A dimethacrylate, vinyl acetate, vinylbutyral, urethane, thiourethane, diethylene glycol bis(allyl carbonate), diethylene glycol dimethacrylate, diisopropenyl benzene, and ethoxylated trimethylol propane triacrylate.

25

27. The article of claim 26 wherein the substrate is an optical element.

28. The article of claim 27 wherein the optical 30 element is a lens.

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29. The article of claim 23 wherein the substrate is an optical element.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/18481

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C03C17/00 C03C17/25 C03C17/42 G02B1/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C03C G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5 116 644 A (ASAII KAZUO ET AL) 26 May 1992 (1992-05-26) cited in the application the whole document ---	1-10,21
A	WO 94 23315 A (BELLEVILLE PHILIPPE ;COMMISSARIAT ENERGIE ATOMIQUE (FR); FLOCH HER) 13 October 1994 (1994-10-13) the whole document ---	1-10,21
P, A	EP 0 884 288 A (NISSAN MOTOR) 16 December 1998 (1998-12-16) claims; examples ---	1-5 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "P" document published prior to the international filing date but later than the priority date claimed

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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

22 December 1999

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## INTERNATIONAL SEARCH REPORT

Interr	nal Application No
PCT/US 99/18481	

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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